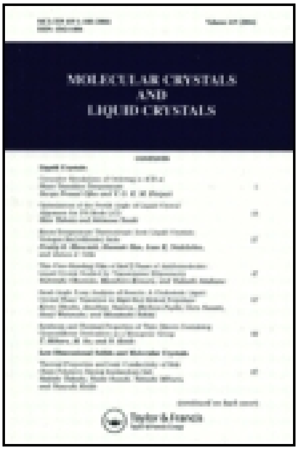

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

New Soluble π -Conjugated Tetrathiafulvalene (TTF) Polymers Bearing Long Alkyl Side Chains: Preparation by Organometallic Polycondensation, Structure and Chemical Properties of the Polymers

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To cite this article: Takakazu Yamamoto, Takayuki Sasaki, Tomoaki Yanagida, Takahisa Shimizu, Isao Yamaguchi, Munetaka Akita, Shintaro Sasaki, Takashi Fukuda & Hiro Matsuda (2002): New Soluble π -Conjugated Tetrathiafulvalene (TTF) Polymers Bearing Long Alkyl Side Chains: Preparation by Organometallic Polycondensation,

Structure and Chemical Properties of the Polymers, Molecular Crystals and Liquid Crystals, 381:1, 101-112

To link to this article: http://dx.doi.org/10.1080/713738732

Mol. Cryst. Liq. Cryst., Vol. 381, pp. 101–112

1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290102044

NEW SOLUBLE π-CONJUGATED TETRATHIAFULVALENE (TTF) POLYMERS BEARING LONG ALKYL SIDE CHAINS: PREPARATION BY ORGANOMETALLIC POLYCONDENSATION, STRUCTURE AND CHEMICAL PROPERTIES OF THE POLYMERS

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New soluble poly(arylene) polymers containing TTF units in a π-conjugated main chain were obtained by organometallic polycondensation. The polymers assume an ordered structure in the solid and are electrochemically active to be oxidized at about 0.3 V vs. Ag^+/Ag in cast films.

Keywords: tetrathiafulvalene; alkyl substituent; π-conjugated polymer; ordering in the solid; electrochemistry

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Received 23 May 2001; accepted 28 June 2001.

The authors are grateful to Prof. K. Osakada, Mr. M. Tanabe, and Dr. T. Morikita of Tokyo Institute of Technology for their helpful discussions and experimental support. This work was partly supported by CREST and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports, Japan.

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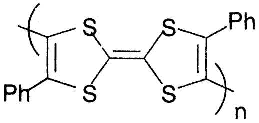
INTRODUCTION

Tetrathiafulvalene (TTF) and its analogues have attracted much attention because their CT complexes show interesting chemical and physical properties [1]. To obtain mechanically tough materials based on TTF, much effort has been devoted to synthesizing macromolecular TTFs, including dendrimeric TTFs and TTF-substituted polyolefins [2–4].

However, reports on linear polymers containing TTF units in a large π-conjugated system are limited [4]. We previously reported the preparation of the following π-conjugated TTF polymer with phenyl substituents [4b].



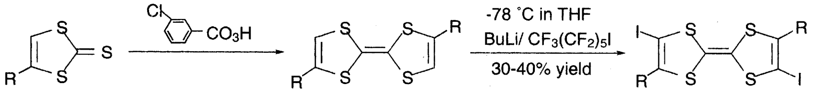
However, in this polymer the bulky Ph substituents seem to disturb intermolecular interactions between the polymer molecules which may be important for obtaining unique chemical and physical properties in the solid.

To expand the chemistry of TTF polymers, and for better understanding of the TTF polymers, we have prepared analogous TTF polymers with alkyl substituents instead of the Ph substituent. Without substituents, the TTF polymer seems insoluble and unprocessable. Introduction of long alkyl substituents is expected to increase the solubility and may lead to ordering of the polymer molecules assisted by side chain crystallization [5]. Here we report results of the preparation of this new class of TTF polymers with long alkyl side chains and chemical properties of the polymers.

RESULTS AND DISCUSSION

Dialkyl-TTFs were synthesized by the homo-coupling reaction of 4-alkyl-1,3-dithiol-2-thione according to a method developed by Bryce and coworkers [6] and iodinated to yield dialkyldiiodo-TTF (**2a**–**2c**) (Equation 1). **1a**–**1c** were isolated as orange crystals, and data from elemental analysis (e.g., for **1c**: Found: C, 64.64; H, 9.18; S, 26.40%.

Calc: C, 64.41; H, 9.15; S, 26.45%) and ^{1}H NMR spectroscopy confirmed these structures.



(1)

1

2

1a R = n-C_6H_{13}

1b R = n-C_8H_{17}

1c R = n-$C_{10}H_{21}$

2a R = n-C_6H_{13}

2b R = n-C_8H_{17}

2c R = n-$C_{10}H_{21}$

However, it was difficult to determine the configuration of **1** and **2** based on the ^{1}H NMR data, and the obtained products may contain *Z*-isomers. Two specimens of **1c** gave the same *E*-configuration and the crystallographic data are: $C_{26}H_{44}S_4$, $M = 484.87$, Orthorhombic, $a = 10.554(6)$ Å, $b = 9.717(3)$ Å, $c = 55.144(7)$ Å, $V = 5655(3)$ Å^3, T = 293 K, space group ***Pbca*** (no. 61), $Z = 8$, $D_{calc} = 1.140\,gcm^{-3}$, no. of used reflections = 1973, no. of variables = 271, $R = 0.060$, $R_w = 0.043$. The obtained product may contain a *Z*-isomer. The two 1,3-dithiole rings of **1c** are slightly twisted with a dihedral angle of about 3°. As shown in Figure 1b, **1c** assumes an ordered structure assisted by the packing of the long alkyl side chains. Crystalline **1c** underwent a transition from a crystalline phase to a smectic liquid crystalline phase at 31°C and showed a smectic-isotropic transition at 51°C, which was revealed by polarized light microscopy. The DSC showed two endothermic peaks at 42°C and 63°C at a heating rate of 10°C min^{-1}. Dihexyl-TFF and dioctyl-TTF did not show liquid crystalline properties, presumably because of insufficient length of the alkyl chain. There are several examples of TTF derivatives which show liquid crystalline properties [7]; however, examples of such derivatives are still limited. No crystal of **2** suitable for X-ray crystallography was obtained; however, the molecule is also considered to assume an *E*-configuration. Indeed, an *E*-configuration was confirmed for a diphenyl analogue of **2** [4b]. ^{1}H NMR and elemental analysis data from **2a**–**2c** agreed with the proposed structures.

Organometallic polycondensations using a zero-valent nickel complex (a mixture of bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$, and 2,2′-bipyridiyl, bpy)[4b] afforded poly(2,6-dialkyl TTF-3,7-diyl)s (**3a**–**3c**) in high yields (Equation 2). For example, **3c** was prepared by using 0.52 mmol of **2c**, 0.95 mmol of Ni(cod)$_2$, 0.97 mmol of bpy, and 1.0 mmol of cod in 10 cm^3 of DMF at 50°C for 24 h.

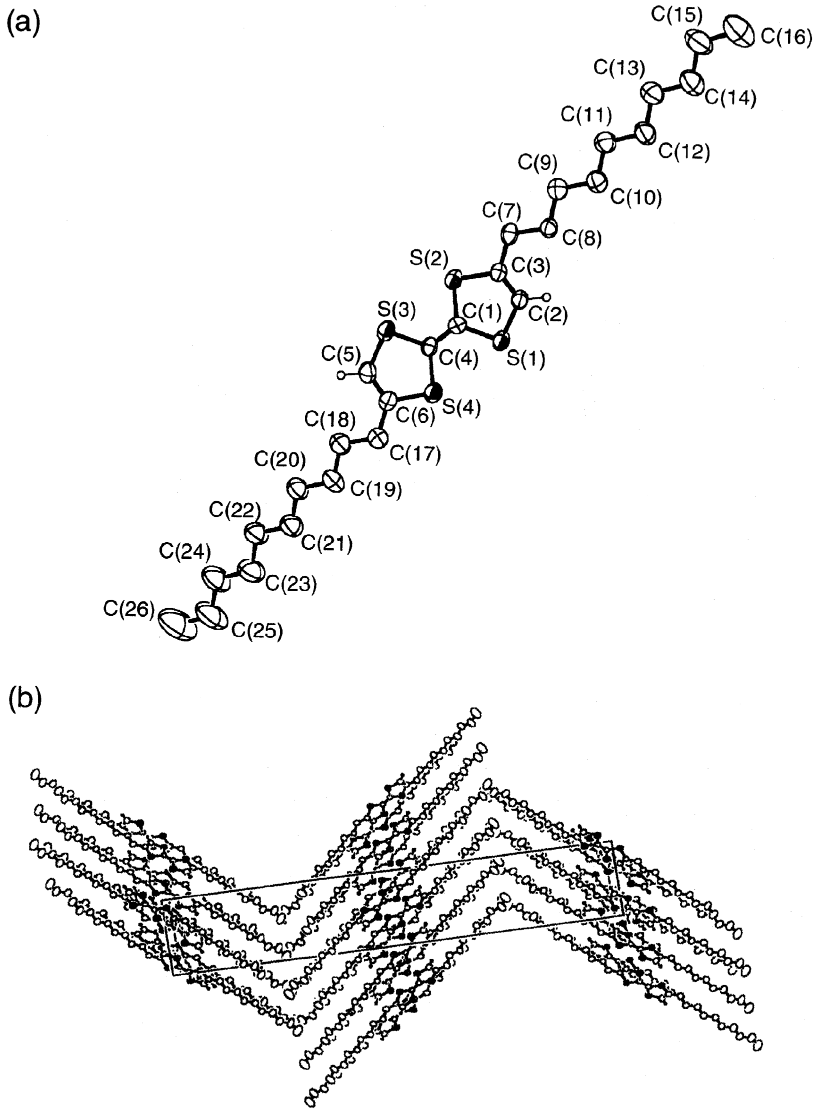
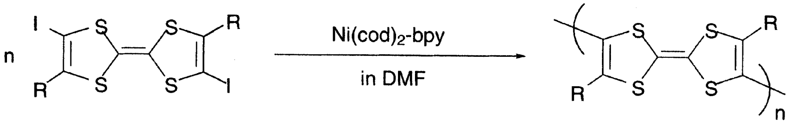


FIGURE 1 ORTEP drawing (a) and stacking pattern (b) of **1c** in the crystal. Selected bond lengths (Å) and angles (deg): C(1)-C(4) 1.331(7), C(1)-S(1) 1.763(7), C(1)-S(2) 1.751(6), C(2)-S(1) 1.736(6), C(3)-S(2) 1.757(7), C(2)-C(3) 1.329(9), C(3)-C(7) 1.503(8), C(7)-C(8) 1.510(1), C(15)-C(16) 1.440(1), S(1)-C(1)-S(2) 114.0(4), S(1)-C(1)-C(4) 122.8(5), S(2)-C(1)-C(4) 123.2(5), C(1)-S(1)-C(2) 94.8(3), C(1)-S(2)-C(3) 96.0(3), S(1)-C(2)-C(3) 119.4(6), S(2)-C(3)-C(7) 116.2(5), S(1)-C(1)-S(2)-C(3) 1.4(4), S(1)-C(1)-C(4)-S(4)-2.8(8), S(2)-C(1)-C(4)-S(3) 3.6(8). Figure 1b is a view along b axis.



(2)

3

3a R = n-C_6H_{13}
3b R = n-C_8H_{17}
3c R = n-$C_{10}H_{21}$

Table 1 summarizes the results of the polycondensation. Polymers **3a** and **3c** were soluble in $CHC1_3$ and THF, whereas polymer **3b** was partially soluble in these solvents. Polymer **3a**, the soluble part of **3b**, and **3c** had number average molecular weights (*M*n) of 3,000, 3,600, and 2,500, respectively, based on GPC analyses (eluent = chloroform vs. polystyrene standards). The *M*n values of **3a** and **3b** correspond to a polymerization degree of about 9. The lower *M*n value of **3c** seems to be due to the low solubility of **3c** in DMF used for the polymerization. Although the polymerization degree is not high enough, the polymer obtained reveals some properties characteristic of π-conjugated macromolecules of TTF with long alkyl side chains.

^1H NMR spectra of **3a**–**3c** (Figure 2) showed a peak due to α-CH_2 hydrogens bonded to the TTF ring at about δ 2.3 and peaks due to other alkyl hydrogens in the range of δ 0.8–1.5. For **3a** and **3c**, an aromatic-H peak at δ 5.8 was also observed and it was assigned to a terminal TTF unit which is considered to be formed from a C-Ni unit during work-up of the polymer [4c]. The peak of the α-CH_2 hydrogens bonded to the TTF unit was somewhat broadened and weakened. Partial natural p-doping of the poly-TTF core (presumably due to oxidation with air) may bring a special electronic state and cause such broadening and weakening. For example,

TABLE 1 Results of Polycondensations

				Solubility[b]				
Polymer	Yield (%)	$10^{-3}M_n$[a]	$10^{-3}M_w$[a]	$CHCl_3$	THF	DMF	Toluene	TFA[c]
3a	95	3.0	3.6	◎	◎	◎	◎	×
3b	79	3.6	42.5	○	○	△	△	○
3c	84	2.5	3.3	◎	◎	×	○	◎

[a] Determined by GPC (eluent = $CHCl_3$, vs. polystyrene standard).
[b] ◎, Soluble; ○, partially soluble; △, slightly soluble; ×, insoluble.
[c] TFA, Trifluoroacetic acid.

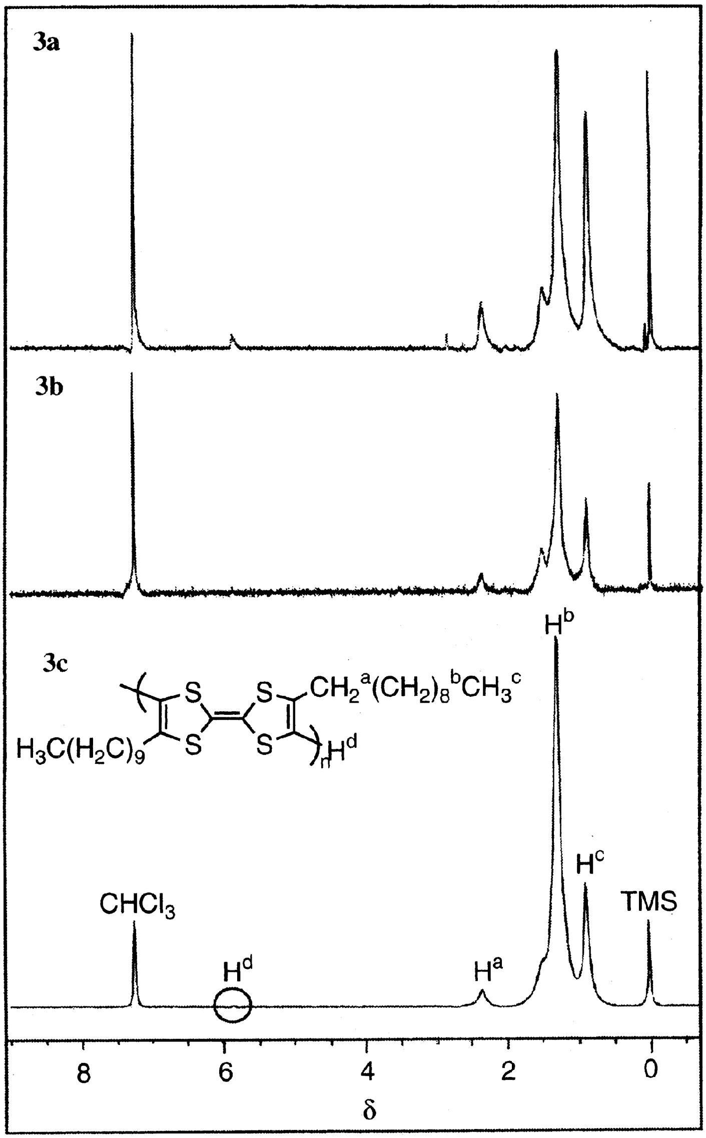
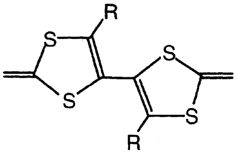
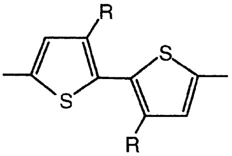


FIGURE 2 ^{1}H NMR spectra of **3a–3c** in $CDCl_3$.

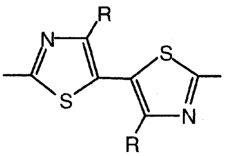
the natural p-doping may render a paramagnetic character to the polymer, which will lead to a great decrease in the ^{1}H NMR relaxation time to broaden the ^{1}H NMR peak(s) of the p-doped part of the polymer. Similar weakening of the ^{1}H-NMR peak in p-doped polythiophenes has been reported [8a,b]. Oxidation of the α-CH_2 group to C=O, which was reported for poly(alkylthiophene)[8c], seem unlikely, since the IR spectrum does not show a peak due to the C=O group. For **3c**, the ^{1}H NMR peak of the α-CH_2 group is especially weakened. This may be due to partial stacking of **3c** assisted by the side chain interaction in the solution [9c]. The local structure of **3** resembles those of regioregular head-to-head poly(3-alkylthiophene) HH-P3RT [10] and poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl) HH-PRBTz [11].



3



HH-P3RTh



HH-PRBTz

Such regioregular five-membered ring polymers often take a stacked structure assisted by the side chain interaction both in the solid and in solution [9c]. When they take such a stacked structure, the α-CH_2 peak in the ^{1}H NMR spectrum is weakened due to loss of free moving of the α-CH_2 unit [9c]. Similar stacking is conceivable for **3**, especially for **3c** with the longest alkyl chain, and this explains the weaker α-CH_2 peak.

For **3c**, the ^{1}H NMR peak area ratio between the CH_3 group in the side chain and the aromatic-H of the terminal TTF unit gave a degree of about 10. IR spectra of the polymers showed a peak at about 1480 cm^{-1} and other peaks in the range of 700–800 cm^{-1}. These peaks are characteristic of the TTF unit and indicate that the TTF unit is maintained in the polymerization.

UV-vis spectra of **1a**–**1c** showed a main absorption peak at 310 nm ($\varepsilon = 9800\,M^{-1}\,cm^{-1}$ in THF) and a subpeak at about 360 nm ($\varepsilon =$ ca. $2500\,M^{-1}\,cm^{-1}$) with an onset of the absorption bands at about 390 nm. The polymers **3a**–**3c** also gave a main peak and subpeak essentially at the same positions; however, the absorption bands were broadened and had long tails extending to about 600 nm, suggesting that there were several overlapped peaks in the range of 390–600 nm that originated from π-conjugation along the polymer chain.

As shown in Figure 3, the powder X-ray diffraction patterns of **3a**–**3c** showed peaks at $d = 16$, 19, and 22 Å, respectively, in addition to a peak at about $d = 4.4$ Å; the peak of **3c** at $d = 22$ Å becomes a shoulder peak in a tail of the strong original X-ray at $2\theta = 0°$. Appearance of the diffraction peak in the low angle region ($d = 16$–22 Å) suggests that the polymers assume an ordered stacked structure assisted by the packing of long alkyl side chains, similar to the cases of regioregular head-to-tail

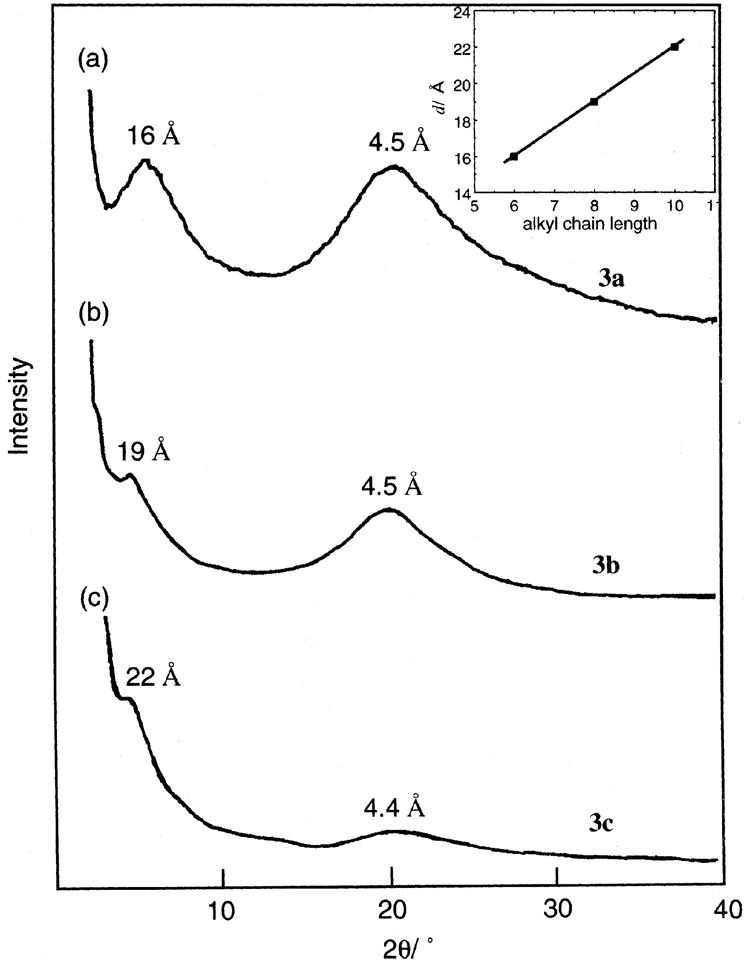
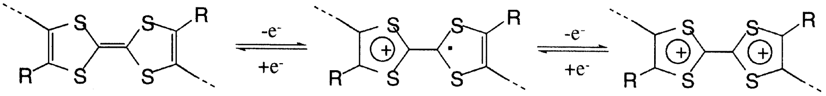


FIGURE 3 Powder X-ray diffraction patterns of (a) **3a** (b) **3b**, and (c) **3c**. Plots of d-spacing between the main chains against the number of carbons in the alkyl side chain.

poly(3-alkylthiophene-2,5-diyl)s, HT-P3RThs [9]. Plots of the *d* value vs. the number of carbons in the alkyl side chain yield a straight line (cf. inset in Figure 3), similar to the case of HT-P3RThs [9]. The straight line has a slope of 1.6 Å/carbon and an intercept of about 6.5 Å. The linear correlation, slope of the linear line, and the intercept suggest [5,9] that (a) the *d* value corresponds to the distance between the poly-TTF core chains separated by the long alkyl side chains, (b) the polymers take an end-to-end packing mode [5] in the solid phase, and (c) the poly-TTF core chain has a thickness of about 6.5 Å. Packing of alkyl side chains of polymers often gives a broad peak at $d = 4.4$ Å, which corresponds to the distance between the chains [5]. Polymers **3a**–**3c** did not show liquid crystalline properties. Thermogravimetric analysis showed that **3a**–**3c** begin thermal decomposition at about 200°C.

All the polymers were electrochemically active, and cyclic voltammograms (CV charts) of their cast films gave two-step peaks at about 0.3 and 0.6 V vs. Ag^+/Ag as shown in Table 2. The peaks are assigned to the formation of radical cations and dications of the TTF unit, as shown in Equation 3.



(3)

As shown in Figure 4, the p-doping and p-undoping peaks of the polymer are broadened compared with those of TTF [12], suggesting delocalization of electron along the polymer chain. Similar broadening has been reported for a TTF dimer with no substituent [12], and the present CV results suggest a higher extent of delocalization than that in another TTF dimer with substituents [13]. In the cast film, the stacking of the polymer molecules assisted by the long alkyl chain may bring about a coplanar structure of the polymer and the delocalization of electron. Although biphenyl takes a twisted structure, poly(*p*-phenylene)s with long alkoxyl groups [14] are considered to assume a stacked planar structure assisted by the side chain crystallization similar to the case of HT-P3RTh [4c,9c].

For **3c**, the oxidation potentials are higher than those of 2,6-didecyl-TTF ($E_{pa} = 0.16$ and 0.42 V vs. Ag^+/Ag). The doping levels (charge stored per repeating unit) estimated from the electric current of **3a** and **3c** were 0.41 and 0.27, respectively. The electrochemical processes are accompanied by color changes (electrochromism) of the film. Neutral polymers **3a**–**3c** are brown, and the color of the films changes from brown to green during

TABLE 2 Electrochemical Data from Films of Polymers

	Peak potential[a]/V			
	E_{paI}	E_{paII}	E_{pcI}	E_{pcII}
Polymer	(p-doping)		(p-undoping)	
3a	0.24	0.64	0.09	0.36
3b	0.35	0.65	0.22	0.37
3c	0.34	0.58	0.30	[b]

[a] Versus Ag^+/Ag. Measured in an acetonitrile solution of $[Et_4N]BF_4$ (0.1 M).

[b] Not observed.

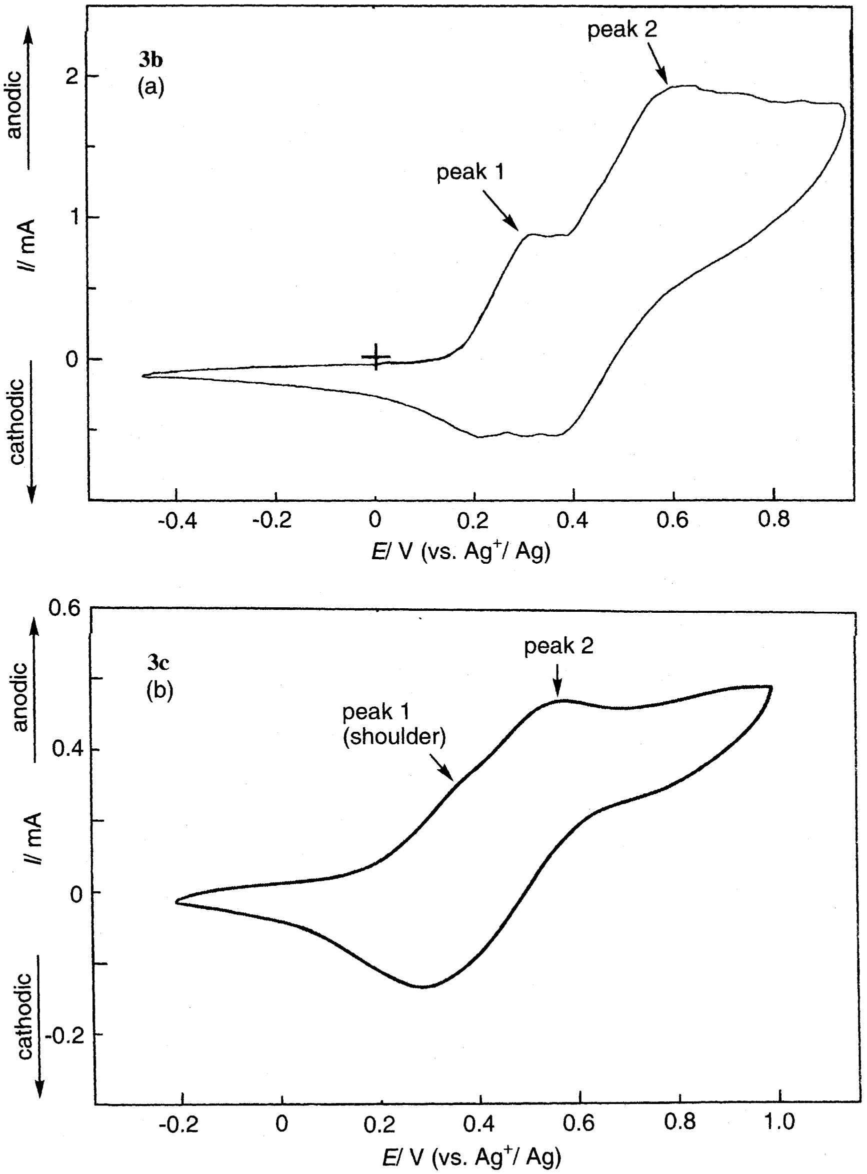


FIGURE 4 CV charts of cast films of (a) **3b** and (b) **3c** on a Pt electrode (1 cm × 1 cm) in a CH_3CN solution of 0.10 M $[NEt_4]BF_4$. $Ag^+/Ag = AgNO_3/Ag$ wire. At room temperature (about 25°C).

oxidation. Polymers **3a**–**3c** themselves showed only a low electrical conductivity σ of below 10^{-8} S cm^{-1}. Iodine-doped polymers of **3a**–**3c** showed electrical conductivities of 6×10^{-7}, 9×10^{-6} and 4×10^{-6} S cm^{-1}, respectively.

As described above, organometalic polycondensation of dihalogenated dialkyl-TTFs gave soluble poly(dialkyl-TTF)s. Although the polymerization degree of the polymers was not high enough, fundamental information about their structures and electrochemical properties was obtained. The monomers in this study can be useful candidates to obtain various types π-conjugated poly(TTF)s by organometallic polycondensation (e.g., cross-coupling polymerization with diethynyl and distannyl compounds).

REFERENCES

[1] (a) Underhill, A. E. (1992). *J. Mater. Chem.*, *2*, 1.
(b) Ferraris, J., Cowan, D. O., Walatka, V. V., & Perlstein, J. H. (1973). *J. Am. Chem. Soc.*, *95*, 948.
(c) Schukat, G., & Fanghanel, E. (1996). *Sulfur Rep.*, *18*, 1.
(d) Otsubo, T., Aso, Y., & Takimiya, K. (1996). *Adv. Mater.*, *8*, 203.
(e) Navor, N. L., Robertson, N., Weyland, T., Kilburn, J. D., Underhill, A. E., Webster, M., Svenstrup, N., & Becher, J. (1996). *Chem. Commun.*, 1363.
(f) Solooli, D., Parker, T. C., Khan, S. I., & Rubin, Y. (1998). *Tetrahedron Lett.*, *39*, 1327.
(g) Yamashita, Y., & Tomura, M. (1998). *J. Mater. Chem.*, *8*, 1933.
(h) Bryce, M. R. (1999). *Adv. Mater.*, *11*, 11.
(i) Yamada, J., Nishikawa, H., & Kikuchi, K. (1999). *J. Mater. Chem.*, *9*, 617.

[2] (a) Hawker, C. J., & Fréchet, J. M. J. (1990). *J. Am. Chem. Soc.*, *112*, 7638.
(b) Bryce, M. R., Devonport, W., & Moore, A. J. (1994). *Angew. Chem. Int. Ed. Engl.*, *33*, 1761.
(c) Wang, C., Bryce, M. R., Batsanov, A. S., Goldenberg, L. M., & Howard, J. A. K. (1997). *J. Mater. Chem.*, *7*, 1189.
(d) Wang, C., Bryce, M. R., Batsanov, A. S., Stanley, C. F., Beedy, A., & Howard, J. A. K. (1997). *J. Chem. Soc., Perkin Trans.*, *2*, 1671.

[3] (a) Kaplan, M. L., Haddon, R. C., Wudl, F., & Feit, E. D. (1978). *J. Org. Chem.*, *43*, 4642.
(b) Pittman, C. U., Ueda, M., & Liang, Y. F. (1979). *J. Org. Chem.*, *44*, 3639.

[4] (a) Bryce, M. R., Devonport, W., Goldenberg, L. M., & Wang, C. (1998). *Chem. Commun.*, 945.
(b) Yamamoto, T., & Shimizu, T. (1997). *J. Mater. Chem.*, *7*, 1967.
(c) Yamamoto, T. (1999). *Bull. Chem. Soc. Jpn.*, *72*, 621.

[5] Hsieh, H. W. S., Post, B., & Morawetz, H. (1976). *J. Polym. Sci.: Polym. Phys. Ed.*, *14*, 1241.

[6] (a) Dhinsda, A. S., Bryce, M. R., Lloyd, J. P., Petty, M. C., Kobayashi, K., & Tukada, H. (1988). *J. Chem. Soc., Chem. Commun.*, 1391.
(b) Dhinsda, A. S., Bryce, M. R., Petty, M. C., Kobayashi, K., & Tukada, H. (1989). *Synth. Met.*, *31*, 379.

[7] Andreu, R., Barbera, J., Garin, J., Orduna, J., Serrano, J. L., Sierra, T., Leriche, P., Sallé, M., Riou, A., Jubauly, M., & Jorgues, A. (1997). *Synth. Met.*, *86*, 1869.

[8] (a) Yamamoto, T., Kashiwazaki, A., & Kato, K. (1989). ***Makromol. Chem.***, ***190***, 1649.
(b) Miyazaki, Y., & Yamamoto, T. (1994). ***Synth. Met.***, ***64***, 69.
(c) Ljungqvist, N., & Hjertberg, T. (1995). ***Macromolecules***, ***28***, 5993.

[9] (a) McCullough, R. D., & Lowe, R. D. (1992). ***J. Chem. Soc., Chem. Commun.***, 70.
(b) Chen, T.-A., Wu, X., & Rieke, R. D. (1995). ***J. Am. Chem. Soc.***, ***117***, 233.
(c) Yamamoto, T., Komarudin, D., Arai, M., Lee, B.-L., Suganuma, H., Asakawa, N., Inoue, Y., Kubota, K., Sasaki, S., Fukuda, T., & Matsuda, H. (1998). ***J. Am. Chem. Soc.***, ***120***, 2047.

[10] Maior, R. M. S., Hinkelmann, K., Eckert, H., & Wudl, F. (1990). ***Macromolecules***, ***23***, 1268.

[11] Yamamoto, T., Suganuma, H., Maruyama, T., Inoue, T., Muramatsu, Y., Arai, M., Komarudin, D., Ooba, N., Tomaru, S., Sasaki, S., & Kubota, K. (1997). ***Chem. Mater.***, ***9***, 1217.

[12] Becker, J. Y., Bernstein, J., Ellern, A., Gershtenman, H., & Khodorkovsky, V. (1995). ***J. Mater. Chem.***, ***5***, 1557.

[13] John, D. E., Moore, A. J., Bryce, M. R., Batsanov, A. S., Leech, M. A., & Howard, J. A. K. (2000). ***J. Mater. Chem.***, ***10***, 1273.

[14] Vahlenkamp, T., & Wegner, G. (1994). ***Macromol. Chem. Phys.***, ***195***, 1933.